



Aging of the photocatalytic TiO₂ thin films modified by Ag and Pt



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ABSTRACT

This work focuses on the investigation of the photocatalytic activity of the TiO₂ thin films (either modified or unmodified by noble metal) and on its stability during 16 months after deposition. RF discharge was used to deposit the TiO₂ thin films by PECVD from the mixture of titanium isopropoxide (TTIP) vapors and oxygen. The surface of TiO₂ films was subsequently modified by Ag or Pt by means of magnetron sputtering. Several analytical methods were used to characterize the thin films properties. XPS was used to investigate the chemical composition of the surface, SEM to study the surface morphology. The photocatalytic activity was expressed in terms of photocatalytic efficiency and it was determined by decomposition of the organic dye Acid orange 7 (AO7). The results show that the enhancement of the photocatalytic efficiency achieved by the modification by Ag or Pt decreases with time, but it is still several times higher after 16 months aging than in case of unmodified TiO₂ layers.

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1. Introduction

TiO₂ is widely used because of its availability, easy manufacturing and handling, non-toxicity, price and also for its ability of photocatalysis. Photocatalytic TiO₂ is used in many branches of industry. Its properties enable it for use in water treatment, antibacterial coatings or so called self-cleaning surfaces. The photocatalytic properties of thin TiO₂ films and their stability is the main interest of the authors of this work.

Photocatalysis is – likewise photosynthesis – the basic process of life on the Earth. Basically, it is conversion of light energy into chemical energy, which is started by generation of the electron/hole pairs in the semiconductor by absorption of photons of UV light. In principle, hydroxyl radicals •OH and superoxide anions •O₂ are generated on the TiO₂ surface from ambient water after reaction with holes or electrons [1]. These radicals are then responsible for the reactions on the surface, which can involve decomposition of the organic matters, changes in the wettability, etc. The effectiveness of the energy conversion can be expressed through the photocatalytic efficiency. The photocatalytic efficiency is dependent on many factors and a lot of effort has been paid to increase the effectiveness of the process. It is possible to use various dopants to increase the TiO₂ photocatalytic efficiency. Doping by organic compounds such as

nitrogen, carbon or sulphur is possible [2]. Most often pronounced organic dopant seems to be nitrogen – interesting literature search on nitrogen doping is given, e.g. by [3]. Addition of noble metals like gold, silver, and platinum on TiO₂ was also reported by many investigators [2,4–9]. TiO₂ modified by metal clusters exhibits reduction in the electron–hole recombination rate due to the Schottky barrier at the metal–TiO₂ interface [10]. The TiO₂ can be prepared in the form of powder (like Degussa P25) or as a thin film, where sol–gel methods or many methods using plasma deposition like CVD, PVD or PECVD can be used. In this work the PECVD was utilized for the thin TiO₂ films deposition.

Many researchers studied the photocatalytic efficiency of TiO₂ and effects of the dopants or noble metal catalysts, but there are only few works considering stability (aging) of the TiO₂ layers (either modified or not). There are some studies focused on the aging of the sol precursor before sol–gel deposition of TiO₂ (e.g. [11–14]), the effect of water and various water solutions (NaCl or humic acid) was studied too [15] as well as the aging in air at elevated temperature [16]. However, these works cover only short term aging in range of days or weeks. The only work from those mentioned above, considering long term aging (more than a month), is [14], where colloidal solutions of quantum sized TiO₂ particles were studied. The long term study of the Ag or Pt doped TiO₂ thin films was not described yet according to the authors best knowledge. In this work we investigate how the photocatalytic efficiency develops with time for various (or none) modifications of the TiO₂ layers. The long term aging (16 months) is considered.

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2. Experimental

2.1. TiO₂ thin films deposition

The deposition of TiO₂ films was carried out in the low-pressure PECVD reactor with planparallel plate electrodes. The closer description of the reactor is possible to find, e.g. in [17]. The bottom electrode was capacitively coupled to the RF power generator (13.56 MHz) via matching unit. The excitation electrode was used as a substrate holder and it was resistively heated to 300 °C during deposition. The temperature was measured by a thermocouple. Liquid titanium (IV) isopropoxide (TTIP) (Ti[OCH(CH₃)₂]₄) was kept in a glass container which was heated to 50 °C. The TTIP vapors were introduced through a needle valve to the upper electrode showerhead and together with the oxygen (fed by a mass flow controller) into the chamber. The flow rate of oxygen was 60 sccm while the working gas pressure was 20 Pa. Bias on the substrate was – 50 V and power delivered to the excitation electrode was 20 W. Glass slides were used as substrates and all analyses were performed with the same samples.

2.2. Modification by Ag or Pt

The TiO₂ films were covered by Ag or Pt. The PVD deposition of the Pt or Ag was carried out on SCD 030 Union FL 9496 (Balzers) by DC magnetron sputtering. The discharge current was 45 mA and target diameter 55 mm. The working gas (argon) pressure was 5 Pa. The samples were placed on the grounded electrode and the deposition time varied from 3 s to 24 s.

2.3. Photocatalytic efficiency measurement

The decomposition rate of the organic dye Acid orange 7 (AO7, formula C₁₆H₁₁N₂NaO₄S) was used to determine the photocatalytic efficiency of the samples. The measurement is described, e.g. in [18] in detail. Basically, glass substrate with the tested film was dipped into 25 ml of AO7 and illuminated by the UV-A lamp (Philips BLB 15 W). The efficiency of photocatalytic decomposition was evaluated from changes of AO7 concentration as a function of irradiation time. The concentration of AO7 was measured by the absorbance at $\lambda = 485$ nm, using spectrophotometer UV-vis (GBC/Cintra2).

For evaluation of the photocatalytic efficiency r we assumed the decomposition reaction runs according to the kinetics of the first-order. Such reaction is described by the Eq. (1)

$$\frac{dc}{dt} = -K_r c_0 \quad (1)$$

where c_0 is initial concentration [mol dm⁻³], c is final concentration, t [h] is irradiation time and K_r [h⁻¹] is reaction rate constant. The solution of Eq. (1) is $c = c_0 e^{-K_r t}$ and then $K_r = \ln(c_0/c)/(1/t)$. The photocatalytic efficiency r is calculated from this constant by considering the volume of the AO7 V [m³], area of the sample S and intensity of the UV irradiation P [W m⁻²]. The photocatalytic efficiency is then

$$r = K_r \frac{V}{SP} \quad (2)$$

as given in [18].

There is no standard method for photocatalytic efficiency estimation. Materials are different (powders, thin films), the experimental arrangements are varying. Various UV light powers, different UV source spectra, different model compounds, different initial concentrations, distance from the UV source are used. Therefore the comparison of the results may be difficult. To overcome above mentioned problems we also related our measurements to well defined compound – TiO₂ layers were prepared by

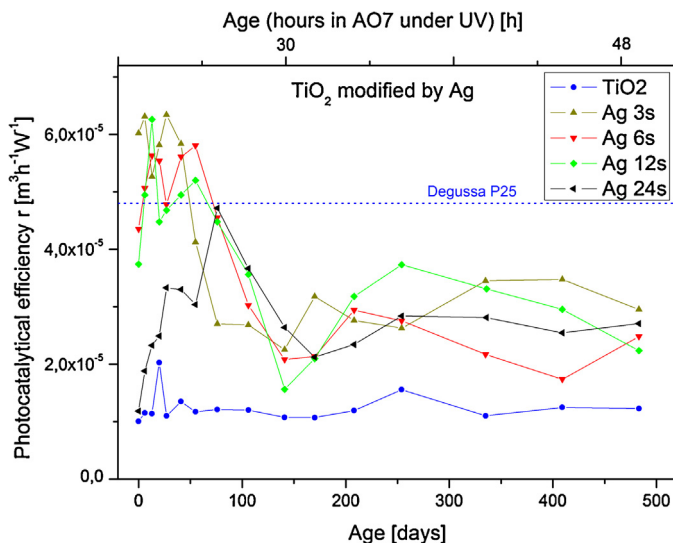


Fig. 1. Changes of the photocatalytic activity of Ag modified TiO₂ layers during 16 months. Standard deviation of the r estimation is smaller than $0.3 \times 10^{-5} \text{ m}^3 \text{ h}^{-1} \text{ W}^{-1}$.

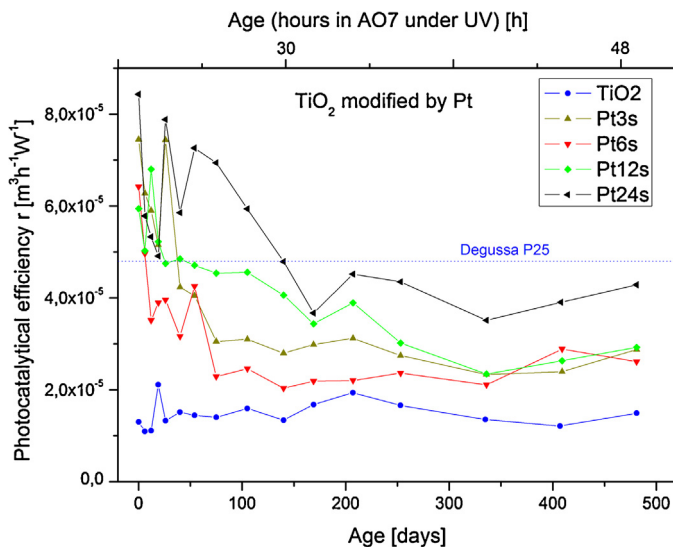


Fig. 2. Changes of the photocatalytic activity of Pt modified TiO₂ layers during 16 months. Standard deviation of the r estimation is smaller than $0.3 \times 10^{-5} \text{ m}^3 \text{ h}^{-1} \text{ W}^{-1}$.

sedimentation from aqueous suspension of Degussa P25 on glass substrates. Sedimented Degussa P25 (1 mg cm^{-2}) shows in our experimental arrangement photocatalytic efficiency $r = 4.8 \times 10^{-5} \text{ m}^3 \text{ h}^{-1} \text{ W}^{-1}$. The value is indicated by dashed line in Figs. 1 and 2, the Degussa P25 was not aged. Another possible photocatalytic efficiency evaluation can also be found in [19–21].

2.4. XPS measurements

The XPS spectra were recorded using hemispherical analyser Phoibos 100 from Specs operated in FAT mode. The spectra were referenced to the peak of aliphatic C–H bonds at 285 eV. Quantification was done from survey spectra recorded at pass energy 40 eV. High resolution spectra were recorded at pass energy 10 eV. Software CasaXPS was used for the spectra processing.

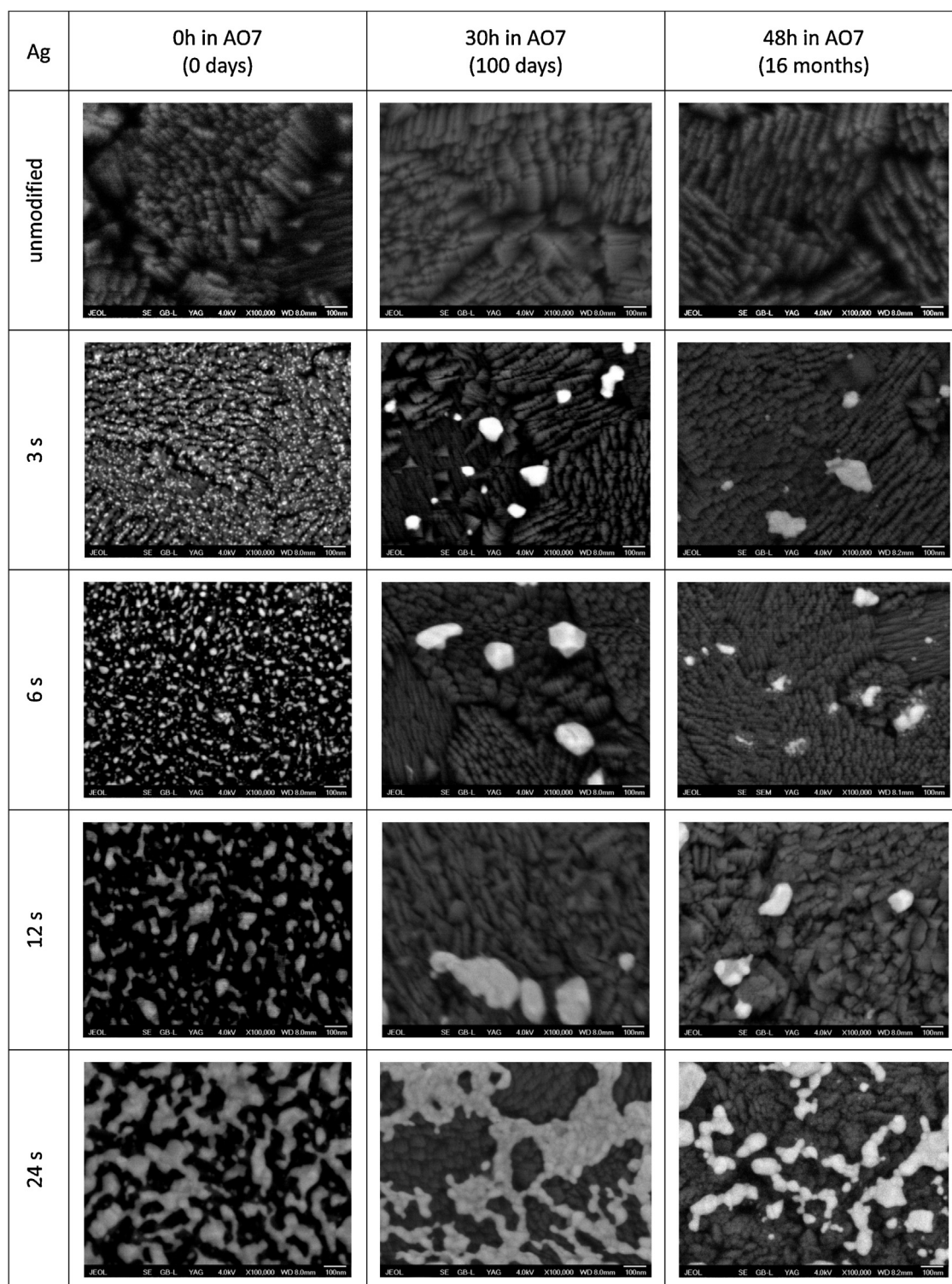


Fig. 3. SEM images of TiO_2 layers modified by Ag. The island-like growth is observed and the coalescence takes place during aging. The scale bars in bottom right corner of each image is 100 nm (i.e. the field of view is approximately $1.2 \mu\text{m}$) and all the images have the same scale.

2.5. SEM measurements

The SEM images were obtained by SEM JEOL JSM-7401F operated in GB mode (gentle beam). The acceleration voltage was 4 kV and magnification $100,000\times$ was used. Secondary electrons were used for imaging.

2.6. Aging of the thin films

The photocatalytic efficiency can be influenced by two factors. One of them is aging and changes related to the aging of the film itself. The other factor is the influence of the AO7 solution. It is obvious, that these factors can not be separated completely, as

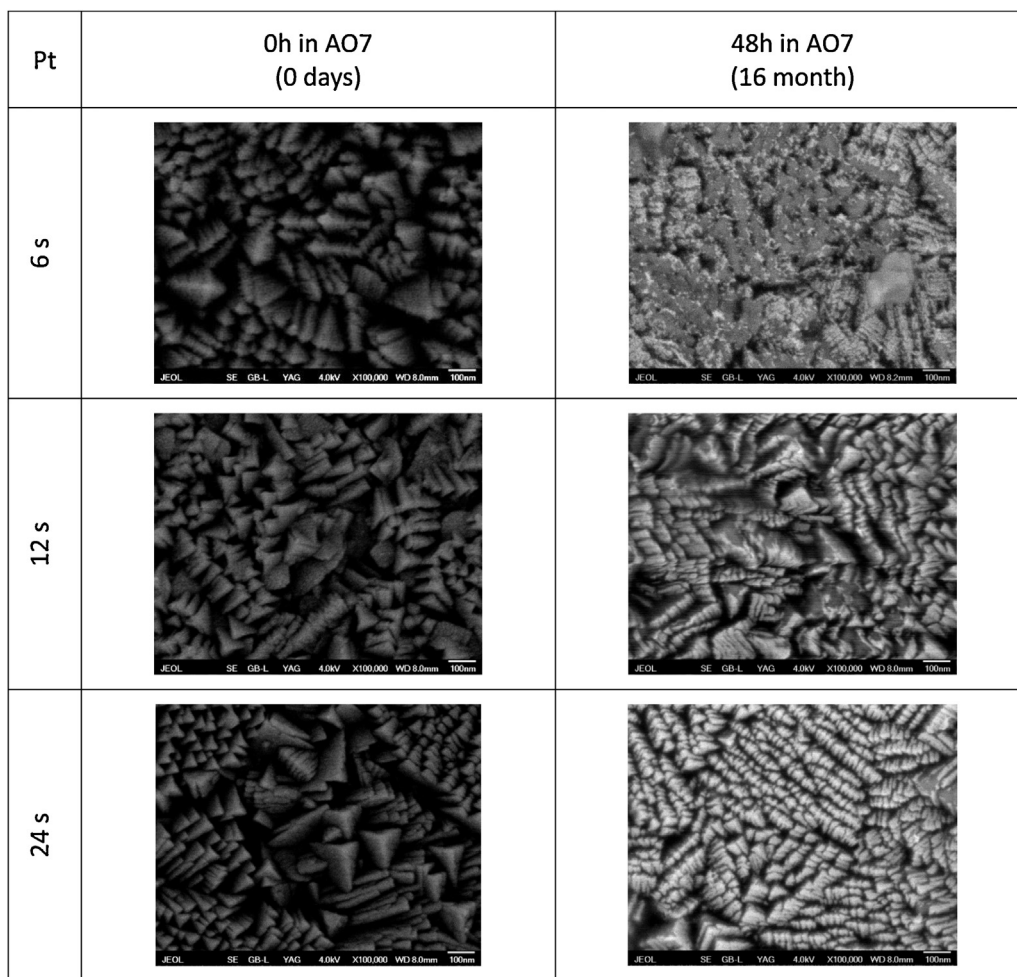


Fig. 4. SEM images of TiO₂ layers modified by Pt. The Pt is smoothly distributed on the TiO₂ surface. The scale bars in bottom right corner of each image is 100 nm (i.e. the field of view is approximately 1.2 μm) and all the images have the same scale.

the photocatalytic efficiency is measured by decomposition of the AO7.

The long term changes of the thin films properties were observed. During 16 months the films were placed 16 times for 3 h to AO7 and irradiated by UV light. After each AO7/UV cycle, the photocatalytic efficiency was measured. The XPS and SEM measurements were also carried out. Firstly the initial state of the samples was measured by XPS and SEM. Second XPS and SEM

measurement was done after 100 days (after first 10 photocatalytic efficiency measurements, i.e. after 30 h of AO7 immersion and UV light irradiation). The third XPS and SEM measurement was performed on samples aged 16 months (in total 48 h of AO7 and UV light exposure) from the Ag or Pt modification. Whenever mentioned, we give both values – the “age” of the samples together with the time spent in the AO7 under UV light. The second SEM and XPS measurement was done after 100 days – not in the

Table 1
Changes of the chemical composition of Ag modified samples with aging as measured by XPS (in % at.).

	Age	Under UV	C1s	O1s	Ti2p	Ag3d
TiO ₂	0 days	0 h	43	45	12	–
	100 days	30 h	47	41	11	–
	16 months	48 h	55	38	7	–
Ag 3 s	0 days	0 h	58	23	3	17
	100 days	30 h	39	46	14	2
	16 months	48 h	47	40	12	1
Ag 6 s	0 days	0 h	49	20	4	28
	100 days	30 h	32	51	15	2
	16 months	48 h	34	48	16	1
Ag 12 s	0 days	0 h	40	16	3	41
	100 days	30 h	28	50	18	3
	16 months	48 h	26	53	18	2
Ag 24 s	0 days	0 h	32	19	3	47
	100 days	30 h	46	30	7	17
	16 months	48 h	35	41	13	11

middle of the observation period. The reason is, that one can expect bigger changes in the beginning of the process (most of the natural processes have exponential progress). The photocatalytic efficiency measurements were carried out more often in the first 3 months as well.

3. Results and discussion

3.1. Photocatalytic efficiency and SEM observations

As seen in Figs. 1 and 2, the efficiency of unmodified TiO₂ films was relatively stable in whole observation time period (16 months). The films with Ag or Pt modification have the photocatalytic efficiency up to 7 times higher compared to unmodified films in the beginning. However, this enhancement holds for about 2 months and then decreases. In case of Ag treatment times 3, 6 and 12 s, the efficiency increases immediately after modification and then decreases with time. When the Ag deposition time was 24 s, the enhancement was almost negligible at the beginning, but after several months the photocatalytic efficiency of the Ag 24 s modified sample increased and the sample behaved equally to the other modification times. This may be caused by the Ag structure on the TiO₂ surface. When deposited, the 3, 6 and 12 s modification results in an island growth of the silver (see Fig. 3), while the 24 s modification covers lot of the TiO₂ surface which decreases the size of the active area and not enough TiO₂ surface is exposed to the ambient. As seen in Fig. 3, after 100 days the coalescence takes place and the spreaded Ag also changes to island-like structure and the photocatalytic enhancement is observed. After 5 months, the photocatalytic efficiency of Ag modified samples stabilizes and the efficiency remains still up to 3 times higher compared to unmodified TiO₂.

When the Pt is used, the result is similar but there are several essential differences against the Ag modification. There is no “burn in” period for any Pt modified sample. Secondly, the SEM images (Fig. 4) show very different structure of the Pt on TiO₂. The island-like structure of Ag is replaced by a smooth coverage by the Pt. The complete removal of the Pt can be excluded due to the XPS measurement – there is about 10% of Pt on the surface after 16 months aging.

3.2. XPS measurements

There were three XPS measurements done with all samples. First measurement checked the initial state of the chemical composition of the layers. Then the samples were tested for their photocatalytic efficiency 10 times, which took 100 days. After these 10 measurements (i.e. after 30 h (integral value) under UV light in AO7) the samples were measured again by XPS. The third XPS measurement was performed after another 6 photocatalytic efficiency measurements, which means in total 48 h under UV in AO7. All the XPS data are listed in Table 1 (silver) and Table 2 (platinum).

The chemical elements present on the surface before any UV light irradiation are C, Ti, O and Ag or Pt respectively. There was N detected on the surface in case of the Pt modification.

The deconvolution of Ti2p high resolution spectra shows Ti2p_{3/2} peak at 459.4 eV (FWHM 1.5 eV). This is in good agreement with binding energies given in the literature for the Ti⁴⁺ titanium (the spectrum is not shown here), e.g. [22]. The Ti2p_{3/2} spectra are the same regardless of the modification used (maximal variation of the peak position is 0.15 eV).

In case of Pt modification, two components N1 and N2 were clearly observed for N1s peak. The example spectra for 12 s Pt modification is shown in Fig. 5. The presence of the two components means, that the nitrogen is bound in two different chemical states.

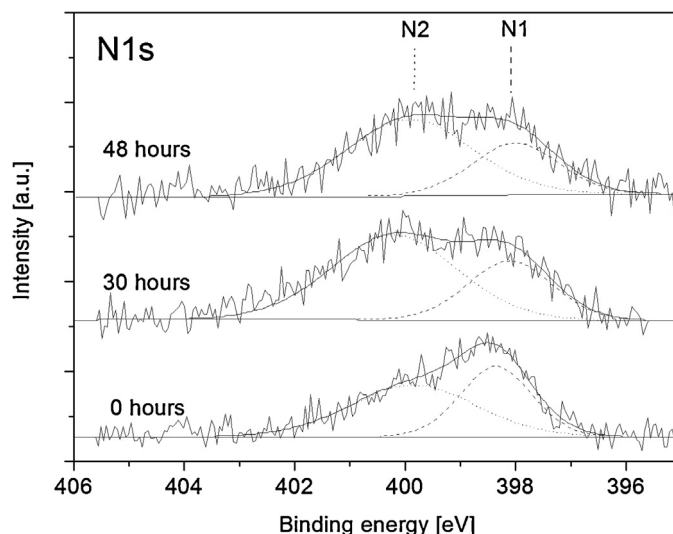


Fig. 5. Development of the N1s high resolution spectra of the TiO₂ thin films modified by Pt (12 s). Dependence on the time spent in AO7 under UV irradiation.

The ratio of the two components changes as the samples are aging – N2 is increasing while N1 is decreasing (or holds the same level). There are at least two sources of nitrogen, which could result in the nitrogen presence on the surface of the layers. The AO7 contains nitrogen, therefore when the AO7 is decomposed by the reaction on the thin film surface, it is possible that the nitrogen is incorporated into the sample or adsorbed on the surface. The two observed components of N1s are located at binding energies 398.2 eV (N1) and 400.0 eV (N2). These values of binding energies are averaged for all Pt modification times. The values covered range from 398.0 to 398.3 eV for component N1 and 399.9 to 400.2 eV for N2. The assignment of these two components is not straight forward as various chemical compounds could result in the two components. The component N1 could be ascribed to nitrogen incorporated into the TiO_x [23] or it can be assigned to Pt–N bonds [24]. The N2 could occur as a consequence of the N adsorbed on TiO_x or NO adsorbed to Pt surface [23,25,26].

We assume, that the Pt presence can play a role in the nitrogen attachment as the Pt is often used as a catalyst for various reactions. Moreover, the TiO₂ surface is relatively rough as can be seen in SEM images and therefore there are many positions suitable for a gas molecule adsorption.

For samples modified by Ag, it was not possible to distinguish whether some small amount of N is present (detection limit is approximately 1% at.) or not immediately after the modification, because the amount of silver is high and the eventual weak N1s peak would overlap with the Ag3d satellite peak. For aged Ag modified layers, the Ag3d peak and also its satellite is weak and the nitrogen is certainly not present on the sample surface in amount detectable by XPS.

Some works showed (e.g. [26]) that N doping shifts the light absorption of the TiO₂ layers toward the visible part of the electromagnetic spectra. Therefore the presence of N in the Pt modified layers possibly may be one of the reasons for higher photocatalytic efficiency of Pt modified layers in long term performance compared to Ag modified samples.

The amount of noble metal on the TiO₂ surface changed as the samples were aging. After 30 h of UV irradiation in AO7 (100 days aging), the amount of noble metal on the TiO₂ surface significantly decreased. The silver content as measured by XPS (Tab.1) decreased to less than 10% of its initial value (initial content was several tens of percent atomic). This can be ascribed to true decrease of the

Table 2
Changes of the chemical composition of Pt modified samples with aging as measured by XPS (in % at.).

	Age	Under UV	C1s	O1s	Ti2p	Pt4f	N1s
TiO ₂	0 days	0 h	28	53	19	–	–
	100 days	30 h	38	49	12	–	–
	16 months	48 h	42	44	13	–	–
Pt 3 s	0 days	0 h	41	33	7	13	6
	100 days	30 h	41	34	9	9	7
	16 months	48 h	47	33	10	7	4
Pt 6 s	0 days	0 h	40	26	6	21	6
	100 days	30 h	44	28	6	14	7
	16 months	48 h	43	33	8	11	6
Pt 12 s	0 days	0 h	41	21	3	29	6
	100 days	30 h	39	23	4	23	11
	16 months	48 h	36	29	7	23	5
Pt 24 s	0 days	0 h	38	15	2	35	11
	100 days	30 h	45	19	1	25	10
	16 months	48 h	37	20	3	29	10

amount of silver (which is, e.g. washed away from the sample by dipping into AO7 solution), but it is also possible that the coalescence plays important role and that simply larger area of TiO₂ is revealed which results in this observation. The coalescence of silver was observed on the SEM images (Fig. 3), but probably both processes are involved.

In case of platinum, the decrease of the metal content on the samples surface due to aging is not so strongly pronounced. After 30 h under UV in AO7 (100 days aging), there is still at least 66% from the initial amount of Pt (more than 9% atomic) on the surface for all Pt modified samples (see Table 2). After another 18 h under UV (48 h in total), both types of modification seem to have the same trend, but still there remains more Pt on the surface compared to Ag.

4. Conclusions

The TiO₂ layers were prepared and modified by Ag or Pt. It was clearly proved, that the modification resulted in enhancement of the photocatalytic efficiency of the thin films – it increased up to 7 times. The short term performance of the layers (photocatalytic efficiency) was better in case of Ag modification, however in case of the long term aging (16 months) the Pt modified samples turned out to be superior.

In case of 24 s Ag modification, different behavior of the sample was observed, which was explained by coalescence of the Ag on the TiO₂ surface. In case of Pt modification such differences were not observed.

The photocatalytic efficiency *r* of all modified samples stabilized after 5 months at the value approximately 3–5 times higher than the efficiency of unmodified samples.

The SEM observations showed, that the silver forms island-like structure that coalesces with aging, on the contrary, the platinum forms homogeneously distributed film, which is structure and also the chemical composition seems to be relatively stable. The XPS and SEM measurements showed that the Ag fades away from the sample surface much faster than Pt during aging.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2014.04.045>.

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